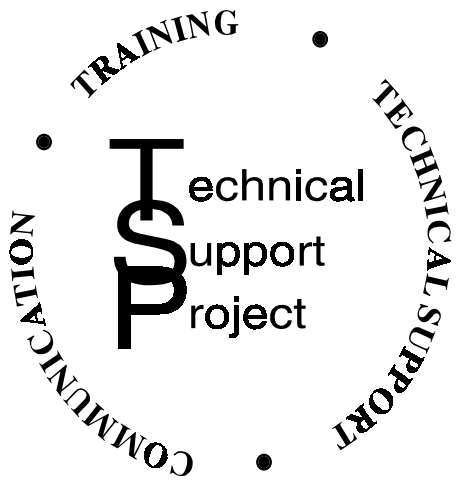
U.S. EPA TECHNICAL SUPPORT PROJECT
SEMI-ANNUAL MEETING

TECHNICAL SESSION MINUTES

July 28-31, 1997
Ada, OK



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Meghan Cassidy, Region 1 • Paul Leonard, Region 3
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MONDAY, JULY 28, 1997

JOINT ENGINEERING AND FEDERAL FACILITIES FORUM SESSION

Natural Attenuation Workshop: Introduction and Basic Principles

Dr. Ron Sims, Director of Utah State University's Water Laboratory, presented an introduction to the basic scientific principles of natural attenuation. He said that the Electric Power Research Institute (EPRI) issued a contract to Utah State, Cornell University, and Atlantic Environmental in 1989 to look into natural processes at coal tar town sites. The three-year study looked into source control treatments followed by natural attenuation (although the term was not in use then). Sims presented a case study of the results of that research, which was conducted at a site in upper New York State.

The site was contaminated with naphthalene, toluene, and acenaphthalene from improperly disposed coal tar wastes during the 1970s, which resulted in naphthalene leaching into surface streams. The site was characterized by a sandy aquifer and NAPL migration. The source encompassed about 1/4 acre, with contamination in the upper 20 feet. About 9600 cubic yards were contaminated over a 7 foot water table. All important ingredients of natural attenuation were present: dilution, sorption, biodegradation, and advection. EPRI's long-term plan, which was based on the scientists' recommendations, called for removal of the coal-tar source, which was accomplished in 1991, and monitoring of the plume through 2001. Sims stressed that monitoring is a integral part of natural attenuation, as is intensive site characterization. EPRI invested several million dollars in the site characterization phase. Dissolved oxygen (DO) is an important parameter to monitor because there is a strong inverse correlation between PAHs and oxygen. After 4½ years, monitoring has revealed significant reduction in naphthalene, although it is not entirely homogeneous.

Cornell and Utah used three criteria published in the 1993 National Research Council's (NRC) publication *In Situ Bioremediation: When Does It Work?* to document natural attenuation at the study site:

1) Demonstrate removal of target constituents at field scale. Since naphthalene and acenaphthalene are more mobile, those two were selected. Phenanthrene is less mobile (closer to the source).

2) There must be microbial potential for bioremediation in the site material. At the coal tar site, ^{14}C-tagged naphthalene and phenanthrene were used to document microbiological potential. Sims's team monitored evolved $^{14}C0_2$ during mineralization of the PAHs.

3) There must be other evidence supporting bioremediation. Sims used metabolic by-products and the reduction of toxicity as determined by MicroTox bioassays to document this. He added that the inverse correlation they found between PAHs and DO are a third supporting factor.

Sims noted that EPRI used its MYGRT model to analyze the data collected by Cornell and Utah. The study demonstrated that contaminant removal followed by natural attenuation is an effective ground-water remediation option and that DO levels are indicative of biodegradation of PAHs. Recent sampling indicates that the contaminant plume is dissipating faster than initially predicted by MYGRT.

In response to a question, Sims confirmed that Cornell University conducted microbial counts in solid and water phases, and characterized the microbes. Predation by other microbes was noticed, and enhanced degradation correlated well with DO.

Another questioner noted that 3,4-ring aromatics are most carcinogenic, and asked if they were considered. Sims said that they looked at high- and low-molecular weight aromatics. There was a concentration of heavier compounds near the source due to the flushing effect of the ground water plume, which dissipated the lighter fractions. The carcinogenic contaminations are disproportionately associated with the heavier fractions. Therefore, source removal tends to remove most of them.

In response to another question, Sims confirmed that they monitored the NAPL blob at the toe of the plume after source removal. Monitoring dissolution of the residual source continues. Sims added that modeling and monitoring were made more complicated by rainfall events that affected dissolution and dilution. He added that the MYGRT model did consider sorption by aquifer solids but not desorption.

Sims's team used “fugacity capacity” to characterize distribution of target PAHs and metabolites. “Fugacity” is a mathematical term very similar to vapor pressure of a gas, and is a measure of the tendency of a chemical to “escape” from a particular place. By contrast, a partition coefficient is a measure of a chemical's affinity for a particular phase. Sims said that fugacity is a simple computation, needing readily available data. A phase concentration equals fugacity times fugacity capacity. Fugacity capacity is derived as follows:

Water	Z_w	1/H (inverse Henry's Law Constant)
Air	Z_a	$1/RT=4x10^{-4}$ (vapor pressure)
NAPL	Z_o	K_{ow} x Z_w (octanol-water partition coefficient x fugacity capacity for water)
Soil	Z_s	Kd x ρ_b x Z_w (partition coefficient x bulk density of soil x fugacity capacity for water)

Original concentrations of PAH compounds and the concentrations of their metabolites in air, water, soil, and NAPL showed that the vast bulk of the contaminants are in the source NAPLs. Therefore, by removing the source mass, one can remove most of the contaminants.

The PAH metabolites serve as “biomarkers” of PAHs; they are much more mobile than the PAHs and migrate more quickly than the original contaminants. Sims noted, however, that some metabolites are more toxic than the parent compounds, so the metabolites need to be monitored as well. Their overwhelming preference for the water phase also means that one need not monitor air or soil concentrations. Cornell and Utah State scientists performed MicroTox evaluations that produced very similar results. Two years after source removal, ground water toxicity (EC_{50}—the amount of source water that reduces microbial activity by 50%) went from 17.5 (*i.e.*, equivalent of 17.5 liters of toxin in 100 liters of water) to non-toxic. In addition, the biochemical metabolites of phenanthrene, found in the laboratory, were first measured in the field during this study.

Sims indicated that one of their goals was to give EPRI a “toolkit” of readily-available techniques and data based upon fugacity analysis. In summary, Sims reported that at the study site after source removal: there was parent compound reduction (step 1 of the NRC criteria); microbial potential (step 2); and other supporting evidence, including DO trends, detoxification, and metabolites (step 3).

Sims explained the mass balance concept for natural attenuation: the fluid phase contains components that can flow (NAPL, gases, water, leachate); the solid phase contains soil organic matter and sand, silt, and clay mineral components. The mass balance determines what percent of the contaminant should be in each phase. Fugacity analysis determines the partitioning of chemicals of concern for direct monitoring, and readily available partition coefficients (K_d, K_{ow}, H) is used to calculate the fugacity parameters. Sims pointed out that mixtures of organic compounds in the ground water will result in a reduction in the aqueous fraction of each organic chemical when compared to the pure chemical's solubility. Raoult's Law (chemical concentration at equilibrium = mole fraction of chemical in organic phase times the aqueous solubility of that chemical) governs the solubility associated with mixtures of organic chemicals. Equilibrium fugacity can be calculated from the known volumes and fugacity capacities of the various phases (soil, water, air, NAPL) and the total chemical mass in the system.

In a saturated aqueous system (below the water table), flow follows Darcy's Law. In an isotropic medium, the hydraulic conductivity (K) is independent of direction; in a homogenous medium, K is independent of location. Dispersion is a nonsteady, irreversible mixing process. In unsaturated soils, K decreases rapidly with water content. Phytoremediation also reduces hydraulic conductivity due to evapotranspiration. Consequently, astute use of natural plantings can help control soil moisture and hence affect bioremediation. The partition coefficient (K_d) is the most important parameter to get right because it has the most effect on diffusion and retardation—more important than bulk density, moisture content, volume, or any other parameter.

Sims also reported that mineralization was significant only with a DO level of 2-5%; there was no degradation without oxygen, and to their surprise, there was reduced mineralization at DO concentrations above 5%. Consequently, he advised that in air sparging situations, DO should not exceed 5%. In response to a question, Sims said that they believed that the 5% DO level was the saturation point for enzymes—equivalent to the oxygen contents typically used in wastewater treatment. He did not know why bioremediation efficiency declined when oxygen levels exceeded 20%.

Sims said that by measuring changes in contaminants and in oxygen, sulfates, nitrate, iron, and methane, independent verification of biodegradation can be demonstrated. He called these “geochemical indicators” of bioremediation. Aerobic biodegradation of nonchlorinated hydrocarbons like BTEX occurs when the microbes respire, and bioremediation is limited by the supply of available electron acceptors like oxygen, nitrate, iron, or sulfate. When the contaminant is a chlorinated hydrocarbon (electron acceptor), bioremediation is limited by the supply of electron donors, and bioremediation occurs through reductive dechlorination. Stochiometric calculations will determine how much contaminant is mineralized.

In response to a question about other oxygen consumers, Sims acknowledged that they use a rule of thumb that about half of the oxygen depletion is attributed to biodegradation and half to other sources. BTEX is more soluble than other electron donors, so is likely to be most bioavailable. He said that the total assimilative capacity should be divided by two to account for this. Sims added that the solubility of many chlorinated compounds, like pentachlorophenol, are highly pH-dependent. Consequently, site-specific pH variability is very important. Also, like many pesticides, pentachlorophenol will ionize.

In conclusion, Sims emphasized three steps in managing natural attenuation: conduct a thorough site characterization; use fugacity to partition contaminants into phases; and use

risk assessment to decide how to remediate. He stressed that the "solution" to remediation will come from an increasingly better definition of the problem.

GROUND-WATER FORUM SESSION

Natural Attenuation Special Topics: Bioscreen 2 Workshop

John Wilson (ORD/NRMRL/SPRD-Ada) provided an overview of Bioscreen 2, which is a program consisting of an Excel spreadsheet macro for evaluating the applicability of natural attenuation to a ground-water plume. It can also be used to verify full-scale models. Version 1.3 can be downloaded from Kerr Laboratory's website (http://www.epa.gov/ada/kerrlab.html); Version 1.4 should be available soon.

Wilson emphasized that Bioscreen 2 is a decision support system and not a model. Bioscreen 2 was developed to evaluate petroleum hydrocarbon plumes, but can be used for plumes of chlorinated solvents as well. It assumes a symmetrical steady-state plume. The program input includes the following types of parameters:

1) hydrogeologic
2) dispersion (which can be field-calibrated or generated from an estimated plume length)
3) adsorption
4) biodegradation (ΔO_2, ΔNO^{3-}, ΔSO_4^{2-}, observed Fe^{2+}, and observed CH_4)
5) general (simulation time, length and width of model area)
6) source data
7) field data (for comparison to Bioscreen 2 results)

Wilson demonstrated the application of Bioscreen 2 for several scenarios; the program calculated the current volume of ground water in the plume and the flow rate of water through the source zone. Wilson began by using data that assumed the natural attenuation of a hypothetical plume involved only dispersion and sorption mechanisms. He proceeded to add input parameters indicative of biodegradation of the plume for comparison. The program generated graphs showing the concentration of contaminants with distance from the source and with time.

Dick Willey (Region 1) commented that if monitoring wells are not located on the centerline of the plume, the sampling results can be misleading because the plume appears to be attenuating, when in reality it is migrating away from the monitoring wells. Wilson acknowledged that incorrectly placed wells can be a problem. He cited a study conducted by a graduate student of Jim Barksdale (Region 4) using chloride as a conservative tracer. The results of the study indicated that the wells have been located incorrectly if the concentrations of chloride in the monitoring wells decrease faster than expected.

Luanne Vanderpool (Region 5) pointed out that use of Bioscreen 2 by the Regions may be limited because many of them do not have access to Excel.

TUESDAY, JULY 29, 1997

JOINT FORUMS SESSION

Natural Attenuation Workshop: Applications and Case Studies

John Wilson (ORD/NRMRL/SPRD/Ada) presented in three hours an abbreviated form of a three-day workshop on natural attenuation of chlorinated solvents in ground water. Materials are available from him upon request. He began with two basic questions for bioremediation —when to start and when to stop—noting that one should halt proactive remediation when it is no longer demonstrating improvement or when it is no faster than intrinsic remediation. He described the basic chemistry of chloroethene biotransformations and dechlorination, described three basic types of sites, how to determine ground water flow and solute transport using geoprobe and other impact technologies, and discussed several case studies. Using these case studies, Wilson described errors associated with using average hydraulic conductivities, the usefulness of microcosm studies to confirm attenuation rates, and the application of rate constants to model bioremediation trends proactively or retroactively. He then described his research into natural attenuation of trichloroethane (TCE) at a jet-fuel site in St. Joseph, Michigan, as a case study bringing together the chemistry, techniques, and principles discussed earlier in his presentation.

Wilson noted that the National Contingency Plan (NCP) defines natural attenuation as a "remedy," but characterized it more as biological containment. Natural attenuation of chlorinated solvents requires low oxygen, low nitrate, high ferric iron, low sulfate, high sulfur dioxide, high methane, low redox potential, high dissolved organic carbon, high temperature, high carbon dioxide, and high alkalinity.

One questioner said that Region 5 has low-permeable tills; the geoprobe technique is hindered by the slowness of drainage into the sampler. Wilson agreed that the geoprobe technology is inappropriate for low-permeable soils. It is designed for homogeneous sands.

Another questioner asked if the autoclaving of control samples might alter the soil structure in the microcosms. Wilson agreed that there was a problem in that regard, but autoclaving remains the best way to sterilize the samples. In response to another question, Wilson acknowledged that they looked into biocides instead of autoclaving for control sterilization. He said that Ada's experts believe that autoclaving is better, but indicated that there was as much "art" as science in the process. The choice also depended upon soil matrix and other parameters.

Wilson confirmed that radiolabelled TCE experiments had been conducted to examine biodegradation products, which resulted in complete mineralization to CO_2. He then noted that microcosm experiments showed faster biodegradation reactions than field-scale experiments due to the disturbance of the substrate and increased homogeneity. Wilson likened the phenomenon to tilling a field to improve plant growth.

Wilson was asked how he distinguished sorption from inorganic transformations in his controls. He said that sulfide production was the key; there was not much sulfide production after autoclaving. He acknowledged, however, that it was not always possible to tell.

In answer to another question, Wilson indicated that they did not attempt to enhance biodegradation with nutrients or other enrichment. At Platt Air Force Base, two percent TCE

was not suitable because the degradation products generate salts that kill the microbes. He would have recommended soil flushing instead of enhanced bioremediation.

In a final question, someone noted that the monitoring transects at the St. Joseph site were conducted over three years, and asked if the comparisons might create errors in interpretation. Wilson agreed that the analysis assumed a steady state, and could offer no evidence either way to support the assumption. He noted that the BIOSCREEN 2 model assumes that the NAPL is in steady state and does not migrate with the ground water plume. He acknowledged that the assumption is not always true.

GROUND-WATER AND FEDERAL FACILITIES FORUMS SESSION

Presentations and Discussions Regarding Natural Attenuation at Federal Facilities

Protocol for Natural Attenuation of Radionuclides and Metals

Fran Kremer (ORD/NRMRL-Cincinnati) reported that she attended a meeting with DOE at Sandia National Laboratories in June. She indicated that DOE is pushing for guidance on natural attenuation of radionuclides and metals, and ORD is planning to begin guidance development in late 1998. She added that she would like to involve the Forums early in the development process and asked the Ground-Water Forum for input on guidance needs.

Willey responded that guidance on the natural attenuation of arsenic, manganese, cadmium, and chromium would be very helpful because in his experience, they are the most common metals found in ground-water plumes. Willey further indicated that guidance on monitoring plumes migrating toward surface water bodies would be helpful too.

Vanderpool asked that the mechanisms of natural attenuation and the appropriate methods for evaluating their effectiveness be described. Kathy Davies (Region 3) suggested that future land use be considered and asked whether there would be any limitations to the future land use of a property at which a metals plume has attenuated.

Hydrogeologic Data

Vanderpool commented that remedial investigations typically do not produce the detailed flowfield information that is required for assessment of natural attenuation. Wilson said that Geoprobe, direct push technology, and Waterloo samplers can be used to measure hydraulic conductivity at numerous field locations, rather than at a limited number of monitoring well locations. He used the analogy of exploring for oil, where geophysics and depositional history are used to position a well. He said that similar exploration principals should be used to position wells in a contaminant plume.

Dissolved Oxygen Measurement

Wilson pointed out that field measurements of dissolved oxygen using electrodes often are not reliable due to operator error, and because instrument calibration measurements are not typically recorded. He suggested using colorimetric kits to measure dissolved oxygen to avoid the problems of electrodes. Wilson said that accuracy and precision of the dissolved oxygen measurements are not as essential as reproduceable data. He prefers the colorimetric kits because they yield quick accurate measurements. He also prefers that redox, rather than dissolved oxygen, be measured to assess the stabilization of purge water.

Ned Black (Region 9) asked whether the colorimetric kits should be used in place of the electrodes. Wilson replied that the colorimetric kits should be used; otherwise, dissolved oxygen should not be measured.

Izraeli asked whether there are any problems with using a colorimetric kit because a flow-through cell is not used and the ground-water sample may be exposed to atmospheric oxygen. Wilson indicated that the introduction of atmospheric oxygen can be avoided if the sample collection tube is placed at the bottom of the flask, and the flask is filled until it overflows and displaces the compromised portion of the sample.

Dissolved Hydrogen Measurement

Wilson explained that proper dissolved hydrogen measurements will indicate whether reductive dechlorination is occurring to the extent possible. Low hydrogen values are indicative of insufficient dechlorination. Wilson noted that dissolved hydrogen measurements should be made within 30 minutes of sample collection; therefore, an on-site laboratory is necessary. He added that he and Barbara Wilson (SPRD-Ada) are developing a sample collection technique that allows for off-site hydrogen analysis. The technique involves sealing the syringe hole with silicone to prevent the infiltration or leakage of gases.

Wilson indicated that the ambient temperature at sample collection time will affect the dissolved hydrogen measurement. He may need to specify an allowable temperature range for the analysis in the SOP. In addition, the samples should be shielded from the sun.

Workshop on Natural Attenuation of Groundwater Contamination

Wilson said that the anticipated product of the upcoming Workshop on Natural Attenuation of Groundwater Contamination in Denver, Colorado (August 19-21, 1997) is a set of ORD issue papers that will recommend the QA/QC necessary to evaluate natural attenuation issues.

Case Study

Wilson presented the KL Avenue Landfill site as a case study for plume characterization. The landfill plume has contaminated several private water wells. Extensive 3-dimensional profiling will be conducted prior to positioning monitoring wells. A branched alkane was selected as a tracer based on the suite of contaminants present at the site. The tracer will be used to document whether a previously contaminated monitoring well is no longer contaminated. Wilson said that he believes site characterization should constitute 30 to 40 percent of the project costs, including remediation.

Rene Fuentes (Region 10) commented that the vertical profiling and tracer approach is reasonable for the purpose of research, but it cannot be implemented at most sites because PRPs are resistant to installing additional wells and paying higher investigation costs. Wilson replied that the burden of proof is on the PRP for showing that natural attenuation is controlling the plume.

Davies asked whether dechlorination of chlorinated solvents would affect the use of chloride as a tracer. Wilson said that the concentration of chloride resulting from dechlorination is insignificant in comparison to tracer concentrations.

Draft Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water

Curt Black (Region 10) mentioned that he was concerned that Figure 2-4 in the draft protocol, which depicts general areas for collection of screening data, may imply that six monitoring wells are recommended for the characterization of a plume. He noted that edits to the figure have been made, and the monitoring well symbol is now labelled as a "representative sampling location." Wilson indicated that the figure is not intended to suggest that only six wells can be used to characterize a plume at a site of any size.

Wilson clarified that the protocol was originally developed to address risk-based assessments for CERCLA sites and was not intended as environmental restoration. He said that a paradigm shift resulted in the consideration of environmental restoration.

Wilson explained that the future of the protocol has three options:

1) It will receive an ORD number indicating it is an ORD report.

2) It will not receive an ORD number and will cease to exist as an EPA document. In this option, neither John Wilson's nor Don Kampbell's (SPRD-Ada) names will appear on the document.

3) The document will be reviewed and re-reviewed until it is acceptable to all involved.

From Wilson's perspective, option #3 is not possible because the contract is overspent and there are no funds to conduct the reviews.

Willey indicated that he expects numerous comments to revision 2 of the draft protocol in order to remove policy-specific language. Davies concurred that the protocol cannot proceed "as is" with language that contradicts EPA policy. As an example, Davies cited the use of the terminology "points of compliance," noting that the entire plume must be considered in Superfund. Fuentes suggested the use of the term "performance monitoring well" instead. Izraeli said that the example of an on-site construction worker as a potential receptor in Figure 2-5 implies that ground water will never migrate beyond the site boundary and that future land use always will be controlled. She added that under Superfund, a site is defined by the extent of contamination, not a property boundary. Ned Black pointed out that the protocol ignores ecological risk, implying that because the site is a military installation, the potential for ecological risk does not exist.

Wilson responded that he will edit the protocol to be consistent with EPA policy. The Ground-Water Forum agreed to compile one set of consistent comments from the Forum members and provide them to Wilson for incorporation into the current draft protocol. The Forum also agreed to contact the Federal Facilities Forum to solicit their agreement on revising the protocol. Davies suggested that the protocol be issued in conjunction with the OSWER directive.

Beta Testing

Wilson noted that beta testing, as requested by the forums, is currently being conducted at three sites:

1) Twin Cities Army Ammunition Plant (St. Paul, Minnesota), which has a large TCE plume;

2) Woodlawn Landfill (Cecil County, Maryland), which has a large vinyl chloride plume; and

3) a solvent recycling facility (Muskegon, Michigan), which has a NAPL plume consisting of toluene and PCE.

He explained that the first two sites were selected for testing because the ground-water plumes are contained in fractured bedrock, which is not currently addressed in the draft protocol.

RTDF Course and Protocol on Natural Attenuation

Kremer reported that the Remediation Technologies Development Forum (RTDF) would like to present a course on natural attenuation to the Regions in the Spring of 1998. However, she said that ORD and OSWER do not want to put EPA's stamp of approval on the RTDF course or the protocol that are being developed. (Without EPA's support, the RTDF name cannot be associated with the course.) Wilson added that private companies participating in the RTDF view the AFCEE protocol as too conservative, so they plan to develop their own protocol. Kremer explained that ORD is suffering from budget cuts and must leverage their available funds. As a result, ORD would like to maintain EPA's participation in the RTDF in order to obtain private sector funding.

The Ground-Water Forum expressed concern to Kremer and Wilson because they were not informed of the RTDF protocol. Fuentes mentioned that he had not heard of the protocol until he was in negotiations at a meeting with the primary authors of the document; he felt that this compromised his ability to negotiate. Vanderpool said that the lack of communication between ORD and the Regions results in the perception that the private sector can use ORD "against" the Regions. Kremer recommended that the Regions contact her or Wilson regarding natural attenuation issues.

GROUND-WATER AND FEDERAL FACILITIES FORUMS JOINT SESSION

Communications Strategy Session with ORD

Scott Marquess (Region 7) chaired a joint session with ORD to discuss the need for a communications strategy and protocol for ensuring timely coordination between the Regional RPM and ORD researchers who may be working at federal facilities where natural attenuation is being considered.

Marquess explained that the Air Force and the Army Corps of Engineers have designated natural attenuation as a "presumptive remedy," and cite Ada's involvement at sites as indicative of EPA endorsement. He added that ORD and the Regions must present a consistent position to these federal agencies. The objectives of the discussion were to (1) have the Forum members learn from ORD how ORD balances the expectations of their

federal-agency "customers" against the expectations of the EPA Regions; (2) develop the framework for a formal ORD/Regional Communications Strategy; (3) clarify specific technical concerns; and (4) discuss mutual objectives of technical-support reviews of documents and recommendations transmitted to the Technical Support Centers by the Regions. Marquess said that the Forums desire better communications and a mutual understanding of the business practices of the Regions and laboratories.

How Laboratories Work With Federal Facilities

John Wilson explained that ORD works with other federal agencies through formal Interagency Agreements (IAGs), which specify the scope of their mutual responsibilities and any financial exchanges. He said that NRMRL has an IAG with the Air Force Center for Environmental Excellence (AFCEE) to support the scientific development and testing of a natural attenuation protocol at Air Force sites. He stressed that ORD is not writing the protocol. Clint Hall, SPRD-Ada's Laboratory Director, added that ORD enters into IAGs only when there is mutual interest that is consistent with the laboratory's mission. ORD is not a "consulting" organization, and its sole interest with AFCEE is access to suitable field sites owned by the military. He said that the Air Force and the Coast Guard reimburse EPA for ORD's activities.

Jim Barksdale (Region 4) said that his Region has provided the Athens laboratory with access to federal sites. The advantage for the laboratory to go through the Region is to ensure coordination between the scientists and RPMs, alert ORD to any site-specific complications, and demonstrate to the other federal agency that the EPA scientists are working with the regulators. Wilson acknowledged that the simplest way would be for the Regions to nominate suitable sites for ORD's selection. Kremer said that ORD sent a request to all 10 Regions about two years ago seeking assistance to locate suitable sites, but there was very little response. She added that there is increasing interest in natural attenuation opportunities. Wilson said that ORD's research is not intended to influence remedy selection, rather to help the site manager obtain necessary data to understand the processes and technologies. He acknowledged, however, that he could see how the research results would flow into the decision-making process.

Marquess asked who SPRD-Ada's "customer" is at the Air Force sites. Hall said that ORD has many "customers"—the Program Offices, Regions, and scientific community. ORD tries to understand how contaminants behave, thereby improving the basis of Agency decisions. Wilson added that various ORD Assistant Administrators have stressed various missions (and "customers") for ORD. Steve Smelling (ORD/NRMRL/SPRD/Ada) pointed out that Ada works for EPA. When on an Air Force project, they are not working for the Air Force—they are scientific partners. Wilson pointed out that SPRD-Ada's work with the Air Force on natural attenuation occupies about 3 FTEs and about $500,000 in ORD funds; AFCEE contributes another $100,000 to Ada directly but has spent over $2 million on their own contractor to provide data to Ada.

Craig Thomas (Region 5) said that the Forums have felt ignored in the past on Ada's natural attenuation protocol research with the Air Force. Wilson said that he did not realize that the Federal Facilities Forum existed until the Dallas conference last winter; he intended no slight and expressed willingness to provide all data to the Regions. Wilson asked the Forum members to provide Regional contact lists for all federal sites. Thomas did not think that would be practical, but suggested instead that ORD to contact any of the Forum members for referral to the appropriate RPM.

Thomas asked Wilson to provide a complete list of sites that Ada used to develop the natural attenuation protocol; he suggested that the data that Ada provided the Air Force were not the same as the data that the Air Force submitted to the Region. **ACTION:** Wilson agreed to submit the list of operating units that ORD visited, as well as the data from those locations, but cautioned that the Air Force may have generated data from other sites that ORD did not visit.

Izraeli said that there was a perception problem with Ada's role with AFCEE on the protocol. She said that the Ground Water Forum had been working with Ada since 1990 to develop a protocol, but that project was dropped by the laboratory. When the Forum saw the Air Force/ Ada product, they felt that Ada had abandoned the Forum as its client in favor of the Air Force. Wilson said that the AFCEE protocol was patterned after the St. Joseph (Michigan) site. The research was made possible due to the Technology Innovation Office's support of the Bioremediation in the Field initiative, because ORD could not afford it alone. Hall pointed out that the protocol would have been no different had it been done with EPA funding alone. It is designed for large plumes and would be overkill for small sites without NAPL sources. Izraeli felt that the protocol needs to state explicitly its context within the CERCLA process, including reference to the nine remedy-evaluation criteria in the NCP.

Meghan Cassidy (Region 1) acknowledged that what the Forums were hearing from Ada was comforting, but she repeated their concerns that the services may be misrepresenting Ada's results. She attributed the tension between the Regions and ORD as stemming from the way that the Air Force is representing the protocol as a presumptive remedy and implicitly endorsed by EPA. She displayed the AFCEE Matrix that has become official guidance for the Air Force and Corps of Engineers, showing that natural attenuation is the stipulated remedy for virtually all situations. She noted that AFCEE has promulgated a policy requiring site managers to prove that natural attenuation will not work before they can select any other remedy. She said that this policy conflicts with the NCP, and by citing Ada's involvement, gives the impression that it has EPA's endorsement.

Cassidy presented a quick overview of the Feasibility Study (FS) process and the nine criteria required to evaluate remedy feasibility. She explained that the FS provides the basis for identifying a preferred alternative, supports the final selection of a remedial action, and provides the basis for the formal Record of Decision. The FS is required to address nine criteria:

Threshold Criteria	Balancing Criteria	Modifying Criteria
• Overall protection of human health and the environment • Compliance with “applicable and relevant alternative requirements” (ARARS)	• Long-term effectiveness and permanence • Reduction of toxicity, mobility and volume through treatment • Short-term effectiveness • Implementablity • Cost	• State acceptance • Community acceptance

Cassidy stressed that how natural attenuation is presented to the public is very important, since many communities see it as a “no action” alternative. She said that the services are not providing necessary responses to required criteria. Specifically, they do not address the “time until remedial action objectives are achieved” (under “Short-Term Effectiveness”), or

"ability to monitor effectiveness of remedy," "ability to obtain approvals from other agencies" (both under "Implementability," and "present worth cost" under "Cost."

The Air Force has not demonstrated any investment or interest in long-term monitoring, and there is a perception that the Air Force sees natural attenuation as something it can walk away from after selecting it. Also, if a state has an approved ground-water protection plan, it has delegated authority on ground-water resources. Working with these states as partners on such issues as planning, remedy selection, and data quality objectives will become increasingly important. On cost, the Air Force is not considering long-term operations and monitoring costs. Regions have signed RODs approving natural attenuation with the assumption that the service would conduct long-term monitoring, only to learn afterwards that the service had no intention of doing so. Cassidy pointed out that a recent Inspector General audit of OSWER and ORD criticized EPA's role in overseeing data collection at other federal sites.

Hall suggested that the Regions' problems seem to be directed at the services, and asked specifically what they expected from his laboratory. Cassidy replied that the Regions do not want to be surprised by ORD's involvement, results, or data. She asked that the laboratories submit their draft workplans, and all their data and results to the Regions at least as early as they send them to the other federal agency. She pointed out also that the RPMs often have historical knowledge and information about the site that they can provide ORD. She wanted ORD to understand that what they may perceive as "research" will be represented by the services as a FS. Wilson expressed considerable surprise that the workplans and data they sent to the Air Force was not shared with the Region. Smelling pointed out that ORD laboratories collect only a small fraction of the data for other federal sites.

Doug Bell (OSWER/FFRRO) suggested that EPA has more issues with the Air Force than with others about how the Air Force tends to misrepresent data. Regions may not become aware of ORD's involvement at Air Force installations until they receive a feasibility study from the service. He stressed that AFCEE's goal is to reduce long-term operations and monitoring costs. EPA is trying to force the Air Force to confirm that any remedy is working properly. While EPA can mandate such monitoring, as a practical matter, EPA cannot enforce it. Consequently, EPA must negotiate these issues with the Air Force.

Hall asked if the Forums felt that the natural attenuation protocol was flawed either technically or philosophically. Bell replied that the concern was not with the protocol itself but in the presumptive selection of natural attenuation by the services. Natural attenuation is a legitimate technology, but just one of many potential remedies that must be considered site-by-site.

One of the laboratory participants noted that the problems the Regions were describing with the Air Force went beyond natural attenuation to a general unwillingness to monitor long-term performance. Paul Leonard (Region 3) acknowledged this; yet noted that the Air Force has "lead agency" status, and therefore has greater flexibility to make decisions and EPA has less.

Don Campbell (ORD/NRMRL/SPRD/Ada) explained that before Ada conducted the site characterization for the Air Force, an Air Force contractor prepared the work plan, which was sent to Ada for comments. Ada would have shared the work plan with the Region, but did not know that the Region was not already involved with the Air Force, and did not know whom to contact at the Region. When the study was finished, the Air Force contractor sent

the final draft report to Ada for comments. He stressed that Ada does not recommend natural attenuation to the Air Force for all sites.

Hall asked if the situation with the Regions and the Air Force would be different had there been no ORD involvement. There was general consensus by the Forum members that it would have been different because the Air Force uses ORD's involvement as a strong bargaining tool and wedge to overcome Regional negotiating positions.

Herb Levine (Region 9) said that it was easy to address instances where RPMs were not aware of ORD's involvement. ORD scientists should contact any Forum member for a referral to the RPM if ORD did not know who the RPM was. Jerry Jones (ORD/NRMRL/SPRD/Ada) said that if the request for site involvement comes through the TSC, they always notify the Region. Kathy Davies (Region 3) concurred, noting that she has received copies of all of Ada's activities in Region 3 that went through the TSC. Izraeli pointed out that the problem arises when the RPM does not initiate the request. Luanne Vanderpool (Region 5) suggested that in some situations, the RPM may be at fault. She said that the coordination between Ada and the RPM at the St. Joseph site is working well.

Communications Strategy

Wilson asked the Forums to develop a “strawman” communications strategy that they would like the laboratories to adopt to improve communications and coordination. Ben Blaney (ORD/NRMRL/Cincinnati) suggested that the strawman could be reviewed by the ORD TSC directors at Las Vegas, Cincinnati, and Ada. There was some reluctance by ORD to commit to a procedure on the spot because not all TSCs and laboratories were represented.

In general, the communications strategy would include three steps:

1) Laboratories would contact the Regions prior to concluding any research arrangements at a federal facility. All coordination would go through one of the TSCs.

2) There would be an early teleconference scheduled by the laboratory and the RPM to obtain the Region's perspectives and discuss objectives or possible problems.

3) The laboratory would provide a draft of its workplan to the RPM for review and comment.

4) Nothing in the strategy would prevent ORD from conducting any scientific research with any cooperating partner.

Vicki Lloyd (OAR/ORIA/Montgomery) pointed out that IAGs may encompass sites in several Regions, that field sites may not be identified until after the IAG is signed, and that the National Air and Radiation Environmental Laboratory is not intended to conduct research, rather to conduct field surveys of radiological data. She added that her laboratory and TSC does encourage communications with RPMs as well as the Region's radiation representative.

ACTION: Jones will initiate a teleconference of all TSC directors and the laboratories to find out if there would be any objections to the communications strategy and to obtain concurrence on the process. Cassidy said that the Forums will draft a strategy and forward it

to the laboratory TSCs for comments. They will also participate in the planning teleconference with the laboratories and TSCs.

Cassidy also asked if the Forums could receive the weekly highlights from Ada. Jim Williams (ORD/NRMRL/SPRD/Ada) indicated that the highlights are available on Ada's Home Page every week.

Jon Josephs (Region 2) said that he is organizing a natural attenuation workshop in Denver August 19-22 to review the AFCEE protocol. Josephs noted that some TSP Forum members are on the planning committee and encouraged anyone interested in commenting on the protocol to contact him with their comments.

Reviews of Technical Support Documents

Davies asked the Technical Support Centers to identify on all technical reviews the names and technical disciplines of the actual authors of the response. She indicated the Regions' desire to know if the opinion and recommendations encompass more than one field of expertise.

Specific Areas of Confusion

Herb Levine (Region 5) listed a number of overlapping activities relating to natural attenuation, and asked for ORD's status and explanation of how these activities are coordinated:

- Ada's work on the AFCEE protocol
- The Remedial Technologies Development Forum (RTDF) protocol
- RTDF's training course on natural attenuation
- Ada's training course on chlorinated solvents
- Cincinnati's training course on chlorinated solvents
- Two Ada fact sheets on natural attenuation
- Jon Josephs's natural attenuation workshop
- OSWER's policy directive on natural attenuation
- ASTM's natural attenuation methods for chlorinated solvents
- Ada's “primer” on microbiology for hydrogeologists
- Ada's “technical guidance” for natural attenuation

Fran Kremer explained that the RTDF activities involve collaboration among ORD, OSWER/TIO, and several private and other federal agencies to leverage resources. The bioremediation group originally intended to focus on research, but has shifted more to outreach activities. ORD and TIO became concerned over the perspective of collaborating with them, so EPA will no longer participate on the protocol or training. The private partners will proceed without EPA's involvement.

Wilson said that the AFCEE/Ada protocol will be reviewed carefully by the Federal Facilities and Ground Water Forums, and they should be free to revise or excise any areas that might conflict with policy or insert any clarifications about suitability for remedies. He said that Ada will then present this revised protocol to AFCEE and allow them to join with Ada under EPA's terms. Otherwise, Ada will not be a co-publisher. He acknowledged that this reflects a change in position for Ada, but stressed that Ada wants to demonstrate its

affiliations. If AFCEE accepts EPA's terms, the protocol will be an published as an EPA document.

Josephs did not feel it was appropriate to include any PRP's name as co-authors of EPA guidance. Davies felt that if the protocol was purely technical, there is ample precedent for joint publication—she cited the Handbook for Groundwater Monitoring and the WasteTech monographs. Jeff Heimerman (OSWER/TIO) pointed out that the protocol represented the best available science. If it is not published by EPA, RPMs and PRPs will be forced to depend on someone else's methods.

Jerry Jones said that Ada's natural attenuation fact sheets are being written by the same people who are involved in John Wilson's three-day workshop on chlorinated solvents—they are almost finished, but are basic and do not address controversial policy implications. Ada's natural attenuation "guidance" was intended as an intermediate product in terms of detail between the protocol and the fact sheets. However, if the protocol is issued separately by EPA, the "guidance" will probably become the EPA protocol. Jones pointed out that the protocol, guidance, fact sheets, and training are all inter-related and somewhat dependent upon the OSWER policy (which has not been finished).

Fran Kremer said Matt Small of Region 9 is involved with the ASTM project to develop a method for natural attenuation of chlorinated solvents. Cassidy and Rene Fuentes (Region 10) pointed out that an Executive Order may bind EPA to compliance with the method, and Ken Lovelace (OSWER/OERR) confirmed that the OERR natural attenuation directive will be consistent with ASTM.

Kremer said that NRMRL/Cincinnati's natural attenuation training is being readied for mid-1998 on ground water, soils, and sediments. It will emphasize ground water because more is known. NRMRL anticipates providing the training to six Regions, with about 400-500 people per Region. It will begin to notify the Regions and coordinate with them as it gets closer to finishing the training course. By the end of 1997, Kremer hopes to publish a natural attenuation screening document for soil and sediments for RPMs. She explained that Cincinnati's training is different from Ada's which is a small-group workshop solely focused on ground water.

Marquess asked where the momentum for natural attenuation is coming from, and Kremer explained that the Agency is receiving pressure from regulated communities. ORD is concerned that the underlying science is inadequate, so it has begun intensive research projects. Kremer felt that ORD is comfortable with ground water but behind in soils and sediments. Davies pointed out that other agencies—NOAA and the Fish and Wildlife Service—that are involved in sediments.

AFCEE Peer Review

Craig Thomas (Region 5) reported that at an April meeting with AFCEE on "peer review," the Air Force identified Ada as part of their peer review team. Thomas explained that the Air Force's use of the term "peer review" implied remedy-selection oversight and approval, not scientific peer review as the term is understood at EPA. Furthermore, Thomas explained that AFCEE requires peer review for all remedies that might cost more than $400,000 (virtually all sites). Thomas asked Ada for an explanation of their involvement with AFCEE.

Jones and others at Ada indicated that there has been no involvement by the laboratory in several years, and that past involvement would have been limited to scientific considerations, not decisions affecting remedy selection. Jones indicated his intent to contact the AFCEE representative to learn what AFCEE intended by identifying Ada's participation on their peer review team. Doug Bell (OSWER/FFRRO) volunteered to be an intermediary to obtain information on the AFCEE peer review program.

ENGINEERING FORUM SESSION

Roundtable Discussion on Thermal Desorption

The Engineering Forum met with five thermal desorption vendors and one U.S. Army Corps of Engineers representative to discuss contract, design, and remediation issues associated with thermal desorption technology. A paper on this discussion is being developed by the Forum and will be published under separate cover from these minutes. For a copy of this paper, please contact the Engineering Forum Co-Chairs: Frank Vavra (Region 3), Steve Kinser (Region 7), or Bob Stamnes (Region 10).

WEDNESDAY, JULY 30, 1997

JOINT FORUMS SESSION

Reactive Barriers Workshop

Site Characterization for Permeable Reactive Barriers

Bob Puls (ORD/NRMRL/SPRD-Ada) presented “Site Characterization for Permeable Reactive Barriers” to the joint forums session. Puls referred the group to a fact sheet that SPRD-Ada recently published on permeable reactive barriers (PRBs). The fact sheet provides a background on the technology, lists six installations at which it has been implemented, and lists contacts and sources for additional information.

Puls indicated that an appropriate site characterization for PRBs involves the measurement of hydrological parameters (such as ground-water flow direction, velocity, and flux) and the assessment of seasonal flow changes and the effects of intermittent pumping of nearby wells. The geologic setting, including depositional environment and stratigraphy, must be understood as well. Puls added that aquifer mineralogy and the concentration of total organic carbon may be used to assess the depositional environment. The measurement of geochemical parameters, such as the concentration of dissolved oxygen, carbonate alkalinity, and sulfate, is also important for site characterization. Puls explained that hydrogen is a preferred electron acceptor, and a high oxygen concentration would result in an increased precipitation of ferric hydroxide. An elevated carbonate alkalinity could result in the precipitation of siderite or calcite, and an elevated sulfate concentration could lead to the formation of sulfide. Finally, the microbiology of the site must be characterized and the presence of aerobic and anaerobic conditions must be assessed. Beneficial effects of biodegradation should be considered, as well as detrimental effects, such as biofouling or the loss of barrier permeability.

Puls noted that useful methods for site characterization include subsurface geophysics and push-tool sampling. The results of these investigations should be mapped and modeled to determine the optimum PRB design and monitoring well placement.

Josephs asked how deep the PRBs can be installed. Puls replied that trenching techniques can excavate a PRB to depths of 40 to 50 feet. He added that there are ongoing pilot studies

to emplace barriers at greater depths. Another participant asked if it is important to locate an impermeable stratigraphic barrier below the PRB. Puls indicated that the an underlying barrier is necessary, otherwise the PRB depth must be over designed.

PRB Design Issues

John Vogan (EnviroMetal Technologies, Inc.) indicated that the factors involved in PRB design include the types of reactive materials, plume characteristics, and installation methods. Vogan listed several classes of ground-water contamination and the corresponding reactive materials used to treat them in PRBs:

organic solvents	zero-valent iron, bimetallic compounds
dissolved metals	zero-valent iron, organic carbon
acid mine drainage	organic carbon
gas derivatives	oxygen-releasing compounds
nutrients	organic carbon

Vogan proceeded to summarize the reactions that occur when treating a ground-water plume through the use of the various materials. He indicated that the inorganic chemistry of the ground water, such as calcium, magnesium, alkalinity, and iron, is also altered by PRBs. Vogan indicated that almost any ground-water modeling program can be used to model the effect of PRBs on ground-water flow, but particle-tracking models are commonly used.

Vogan discussed several types of PRB designs, including continuous reactive walls, which extend across the entire plume; funnel and gate, which consists of a low-permeability funnel and permeable treatment gate; and alternative designs, such as *in situ* reactors or the GeoSiphon cell developed by the Westinghouse Savannah River Company. Vogan indicated that above-ground reactive systems can be used but the effect of oxygenating the pumped water must be assessed.

Mallott asked what the typical duration of column tests are to evaluate the effectiveness a PRB material. Vogan said that a steady state is usually reached after 50 pore volumes have passed through the column. This can take three weeks or three to four months, depending on the flow rate and permeability of the reactive material. Mallott asked if there are average degradation rates that can be used in place of conducting column tests. Vogan indicated that enough degradation rates have been calculated for commonly-tested contaminants such as TCE and PCE. Kremer questioned whether the source of zero-valent iron would have an effect on degradation rates. Vogan replied that the milling of the iron filings will certainly have an effect on the rates.

Compliance and Performance Monitoring

Puls indicated that compliance and performance monitoring of PRBs is driven by regulatory requirements; the focus of the monitoring program is on the site and compliance points. Puls explained that 2-inch diameter monitoring wells with 20- to 30-foot screens are typically used for compliance monitoring. The screen is set so that a sample can be collected from the targeted zone. Low-flow sampling techniques are typically used to minimize drawdown. The monitoring wells are positioned upgradient, downgradient, and cross-gradient of the plume as well as under the PRB. Puls indicated that caution must be used when sampling wells near or under the PRB to avoid pulling water from within the barrier.

Puls emphasized the importance of compliance monitoring by citing an example of a site in Elizabeth City, North Carolina at which some cis-DCE and vinyl chloride seeped through the PRB. The concentrations of vinyl chloride exceeded the MCL. Puls added that compliance monitoring should include general water quality parameters, such as cations, metals, anions, pH, dissolved oxygen, and specific conductivity. He indicated that State of North Carolina also requested TCLP testing of the PRB reactive materials to ensure that no new contaminants were introduced to ground water. Puls noted that compliance monitoring at the site has indicated that no sulfate or sulfide is emerging from the PRB. These anions may be absorbing to the zero-valent iron or precipitating and clogging the barrier. Biofouling may also occur.

Puls indicated that monitoring wells can be used for performance monitoring, but preferably with multi-level samplers. The wells are usually sampled using passive or semi-passive techniques. Performance monitoring wells should focus on the immediate vicinity of the PRB. At the Elizabeth City site, a 2-inch diameter well was installed in the wall. Dedicated pumps were used to sample the well, shortening the purge time and limiting the area sampled so that only the water inside the PRB is sampled.

Puls referred the workshop participants to DMLS, a commercial passive multi-layer sampler available through Johnson Screen. Puls explained that the DMLS is available in a 2-inch and 4-inch model. It consists of a series of PVC dialysis cells that are loaded with water and inserted into the screened interval. The cells are later withdrawn for chemical analysis. The DMLS is suitable for low permeability aquifer materials and results in a minimum disturbance of the aquifer and a high resolution of the plume. No purging is required for the DMLS, and it is adaptable for sampling mobile colloids. The DMLS can also be used to estimate the vertical variation in ground-water flow velocity.

Performance monitoring devices should be positioned to verify that there are no leaks from the PRB. Geophysics also can be conducted to ensure proper PRB emplacement. A conductivity probe can be used to confirm “cleanup” since the conductivity between the aquifer and the zero-valent iron differs by over two orders of magnitude.

Puls mentioned that bromide tracer tests can be used to evaluate the hydraulics of the PRB treatment system. It is possible to predict the appearance of a bromide tracer within 15 percent. At Elizabeth City, the tracer revealed that the ground-water flow velocity was 10 to 12 cm/day, which was close to the predicted value, and 20-24 cm/day through the PRB.

Puls noted that the reactivity of the PRB can be evaluated by measuring geochemical indicator parameters, changes in general water chemistry, surface precipitates, and other indicators. Puls said that scanning electron microscopy can be used to examine surface precipitates. A mixed chromium-iron hydroxide precipitate was identified at the Elizabeth City site.

Sean Hogan noted that an aquifer may consist of layers of varying hydraulic conductivity. He asked whether PRBs isolating the permeable layers could be installed. Puls replied that this was done at Elizabeth City; however, he cautioned that the plume and stratigraphy must be well-characterized to use this approach.

Mallott asked whether performance monitoring is necessary at non-test sites. Puls explained that the amount of performance monitoring declines over time at a site and with the technology as a whole. He indicated that a lot of performance monitoring is needed initially

at a site. He added that one should anticipate that compliance monitoring is always needed and that some level of performance monitoring that declines over time will be required. In response to a question from Doug Bell, Puls indicated that the design life of a PRB cannot be estimated yet.

Field Scale Systems

Vogan indicated that six pilot scale and six full scale PRB systems have been installed at sites. The treatment costs for these systems range from $435K to $2.1M. Factors affecting the cost include construction and the reactive iron used for the wall. Construction costs vary based on dewatering needs, material placement, health and safety precautions, unforeseen conditions, water and soil disposal, disruption of site activities, and other factors. To save costs on reactive iron at one site, the iron was placed at the bottom of the flow zone, and high-density polyethylene was placed in the upper zone to direct water toward the iron. Vogan said that the cost of a PRB system can be comparable to enhanced bioremediation.

Vogan cited the Waterloo Field Trial in 1991 as the first field scale system. The system's PRB consisted of 22 percent iron and 78 percent coarse sand, and was not oriented at an angle of 90 degrees to the plume axis. The field trial resulted in the decrease of PCE and TCE and the increase of chloride in ground water. Some DCE was detected in the treated ground water, but vinyl chloride was not. There was no indication of significant precipitation or biofouling.

Vogan said that PRBs less than 50 feet deep can be constructed by trench box, continuous trenching, *in situ* reactors, caissons, and GeoSiphon cell methods. For depths greater than 50 feet, jetting techniques, mandrel/tremie tube, hydrofracturing, soil mixing, and modified slurry wall methods can be used.

Vogan mentioned that the RICE Consortium is funding the investigation of sequenced treatment zones, which combine granular iron with other *in situ* technologies. He cited the example of sequenced treatment zones at the Naval Air Station-Alameda, which used an iron PRB zone followed by a biosparge zone.

The operation and maintenance of a PRB system involves rejuvenation, which may consist of mechanical restoration, closed-loop flushing, or replacement of the affected section. Vogan indicated that rejuvenation must be conducted every five to ten years in most environments. He added that although precipitates may decrease the permeability of the PRB, research has shown that the iron remains reactive.

Sean Hogan (Region 9) asked what problems may be associated with rejuvenating the iron. Vogan indicated that no technique has worked well to rejuvenate the iron. Acid solutions must attack the carbonate, but not the iron. Mechanical means of rejuvenation, such as high pressure jetting or use of solid stem augers to loosen the iron, may be feasible and less expensive than chemical means. Puls clarified that sampling data has not shown much precipitate buildup in the PRB systems thus far. Vogan pointed out that the need for a cost estimate for rejuvenation arises when preparing a 30-year cost comparison with other treatment technologies.

Josephs asked what types of barriers are good for treating carbon tetrachloride and whether bimetallic compounds can be used to treat dichloromethane. Vogan indicated that zero valent iron works for carbon tetrachloride, but not several of the other chlorinated aliphatic

compounds. He said that bimetallic compounds may work to treat dichloromethane, but are expensive to use.

In response to a question on the life span of the PRB system, Puls indicated that it had to be proven that trivalent chromium would not be oxidized to hexavalent chromium at the Elizabeth City site. In addition, it had to be shown that a significant amount of manganese oxide was not present because it can reoxidize trivalent chromium.

Elizabeth City Permeable Reactive Barrier Case Study

Bob Puls discussed remediation work being conducted by NRMRL/SPRD-Ada at an old hard-chrome plating facility located on the U.S. Coast Guard Support Center near Elizabeth City, NC. A field test was conducted in September 1994 at the site to evaluate the *in situ* remediation of ground water contaminated by hexavalent chromium using a permeable reactive barrier. This field-scale test was successful and a full-scale implementation of the technology began in late spring 1996.

The field project involved the installation of 200 linear feet of zero-valent iron filings as a permeable treatment wall downgradient from a thin and shallow TCE and chromium plume, which had begun to migrate off the base into the tidal waters of Albemarle Sound. The wall was composed of two kinds of iron-metal (one from Ada Iron and Metal in Ada, OK, and another from Masterbuilder's Supply in Streetboro, OH) coarse uniform washed sand, and native aquifer material. In addition to the TCE and chromium, chlorinated organic compounds, such as trichloroethylene (TCE), cis-dichloroethylene (c-DCE), and vinyl chloride were also present and slated for treatment by the wall. Performance monitoring of the wall was conducted to evaluate changes in contaminant concentrations and aqueous versus solid phases, analyze hydraulic changes, and examine mass balance and degradation pathways. The following results were seen:

- decrease in Cr(VI) concentrations
- increase in Fe(II) concentrations
- decrease on Eh
- slight increase in pH levels
- decrease in dissolved oxygen
- presence of sulfides only after treatment
- decrease in sulfate concentrations
- increase in alkalinity, I addition, results showed that some natural attenuation of the contamination was occurring, but it was not sufficient to clean up the site.

Bob Stamnes (Region 10) asked whether there was any fluctuation in the River/Tidal plane. Puls said there had been and that they had been trying to get funding to examine how this affects the site. Stamnes then asked how deep the wall can be placed. Puls noted that they received three bids from vendors; one could go as deep as 20 feet, the one chosen could go down to 24 feet, and another could go down to 26 feet, but was not wide enough for the site.

Neil Thompson (Region 10) asked how much tide change occurs at the site. Puls noted one foot at the maximum. Thompson then noted that in Region 10, 12 foot tidal changes can occur, which causes dampening quite quickly.

In response to a question, Puls noted that they did not compact the iron filings; they were poured directly into the wall.

Reductive Dehalogenation of Chloroethene in the Subsurface

Guy Sewell (ORD/NRMRL/SPRD-Ada) presented a discussion on reductive dehalogenation of chloroethene. He explained that this process is based on use of anaerobic transformations, which require electron donors (contaminants) and electron acceptors (*i.e.*, metals and sulfates) to drive the process. Sewell noted that since most contaminated areas do not have uniform distributions of hydraulic conductivity or contaminants, one can use a dual tracer system using injections of bromine and iodine to examine the different layers of the subsurface. An injection and extraction well can be installed to force flow through low-flow contamination layers using horizontal wells.

The system has been successful at decreasing concentrations of vinyl chloride, methylene chloride, cis1-2 DCE, ethene, and TCE. A decrease in toluene, however, has not been seen, but researchers believe that this is because toluene helps drive the dehalogenation process. Ethane concentrations appear to stay constant over time when using this technology. The technology costs approximately $50,000, not including analysis. It has already been demonstrated at DOE's Pinellas, Florida, site.

Jon Josephs, Region 2, asked whether DOE is still operating the system at Pinellas and if so, what is projected to happen when it is shut off. Sewell noted that the pilot already has been shut down and the site belongs to Pinellas County. There has been some discussion about continued pump-and-treat, bioremediation, or a combination of these two technologies, but DOE will decide. There are plans to retest the cluster wells to see if there is a rebound of contamination. The goal is to obtain performance data only, not to run the system through completion.

Sean Hogan asked whether the system is ready for full-scale application. Sewell said yes, noting that DuPont has had success with the system already. However, there has been some criticism about lack of data.

Bob Puls asked whether the system has had different results for different contaminants and concentrations of these contaminants at different depths. Sewell said that this has happened due to injection of electron donors. In response to a question from Dick Willey, Sewell noted that there has been some indication of natural attenuation occurring at the site.

Enhanced Bioremediation for Petroleum Hydrocarbons: Treatment Strategies

Steve Hutchins (ORD/NRMRL/SPRD-Ada) noted that natural attenuation may not occur at rates fast enough to achieve regulatory standards. Therefore, it needs to be examined in conjunction with other technologies. Hutchins then noted that both active remediation and natural attenuation require thorough site characterization to determine if a particular technology will work at a site. For example, if natural attenuation is being considered, one needs to determine if there is a sufficient microbial population in the subsurface for natural attenuation to occur. Hutchins then noted that even if sufficient microorganisms are present, natural attenuation rates still may not be sufficient to remediate a site within a particular set of time. Hutchins then presented a few case studies where natural attenuation has been used in conjunction with active remediation.

The first case study presentation was for a United States Coast Guard Site in Traverse City, MI, where a 10,000 gallon petroleum spill migrated off site to Grand Traverse Bay. Natural attenuation was occurring at the site, but at too slow of a rate. Therefore, an interdiction

field was installed. Active remediation was implemented upgradient of the field, and natural attenuation was allowed to take over downgradient of the site.

The second case study was conducted at a site in Park City, Kansas. Here, a pipeline leak created a five-acre contaminant plume. The site was metabolically active but natural attenuation still was not occurring fast enough. To address the problem, a drinking water well was shut down, and the area is currently undergoing active remediation.

The third case study was for a site that implemented what Hutchins called "Facilitated Natural Attenuation," or FNA. He explained that this is an "in-between" technology that implements both natural attenuation and active remediation. The goal of this study was to mitigate some of the site contaminants and then allow natural attenuation to proceed. The objective was a low cost, low maintenance, and low technology process.

The study was conducted at a site with a fuel contaminated aquifer. Active remediation consisted of a reactive barrier wall, sprinkler systems, and phytoremediation. During the first four months of the study, not much biodegradation occurred due to plant growth and decay. However, sod was removed from areas of intense contamination to facilitate the process of getting nitrate into the subsurface to drive biodegradation rates.

ENGINEERING AND FEDERAL FACILITIES FORUMS SESSION

Phytoremediation: Principles and Case Studies

Bruce Pivetz, ManTech, presented the Forums with an overview of the wide-range of phytoremediation technologies, including phytodegradation (degradation within plants), rhizodegradation (degradation within roots), phytovolatilization (transpiration and volatilization by plants), rhizofiltration (immobilization in the root zone) and phytoextraction (metals uptake into the plant). He explained that phytoremediation is the direct or indirect use of green plants for the *in situ* or *ex situ* remediation of contaminated soil, groundwater, surface water, wastewater, or air. It is an emerging technology that might be an effective, low-cost remedial alternative at many hazardous waste sites.

Pivetz explained that phytoremediation can be used for hydrologic control and soil stabilization. It also can provide a "vegetated" cap or be used as a natural attenuation technology. Phytoremediation can be used to remediate organic contaminants, such as pesticides, chlorinated solvents (TCE), petroleum hydrocarbons (BTEX), PAHs, PCP, PCBs, and munitions (TNT, RDX, and HMX); and inorganics, such as such as heavy metals, nutrients, radionuclides, and selenium. In addition, preliminary research suggests that phytoremediation may be successful at remediating mixed organic waste and metals contamination.

Pivetz noted that full-scale implementation of all forms of phytoremediation has not yet been accomplished. Since it is an emerging technology, most work in phytoremediation has been at the research level in the laboratory or on small-scale field plots. Pivetz then noted that research experience with remediation of metals is more extensive than for other types of contamination. Less work has been done with phytoremediation of organic compounds, although some laboratory or field experiments have been conducted with contaminated soil from Superfund sites.

EPA's SITE program has conducted four pilot studies:

- Carswell Air Force Station in Fort Worth, TX for remediation of TCE in ground water using poplar trees
- Chevron fuel terminal in Ogden, UT, for remediation of TPHs in soil and ground water using poplars, alfalfa, and fescue
- Magic Marker site in Trenton, NJ, for remediation of lead using *Brassica juncea*
- McCormick & Baxter Superfund site in Portland, OR to remediate PAHs and PCP in soil using ryegrass.

The Petroleum Industry also has conducted some pilot studies using phytoremediation to clean up petroleum contamination.

Pivetz noted that a Remediation Technologies Development Forum (RTDF) for Phytoremediation of Organics is now in place. Its purpose is to bridge the gaps between research, application, and regulation. Three workgroups have been established to address TCE in groundwater, TPH/PAHs in soil, and vegetative caps. Information on this Forum can be found on the RTDF website at **http://www.rtdf.org**.

In summary, Pivetz noted the following:

- The specific processes and design considerations for phytoremediation vary greatly depending on the contaminant type and matrix.
- Selection and use of an appropriate plant is critical.
- Depth of soil remediation is likely to be limited by the depth of the plant roots.
- Phytoremediation may be most appropriate for low contaminant concentrations and long time frames.
- Practical implementation of phytoremediation will require more information on techniques, costs, and integration of phytoremediation with other remedial technologies.

GROUND WATER FORUM SESSION

Monitoring for Integration of Hydrologic, Biologic, and Chemical Characterization, Site Characterization Methods

Steve Acree (ORD/NRMRL/SPRD-Ada) indicated that difficulty in site characterization arises due to site heterogeneity, ranging from the microscopic to megascopic scale, of the subsurface. There are several tools to characterize geology, such as continuous geologic logging, grain size analysis, and cone penetrometer testing. Tools to characterize hydrology include pumping tests, slug tests, lab permeameter tests, borehole flowmeters, tracer testing, and grain size analysis; geophysical tools include surface and borehole geophysical logging and electromagnetic conductivity tests.

Acree noted the advantages of borehole flowmeters. They greatly increase one's knowledge of the subsurface, yield data rapidly, and fit into existing 2-inch diameter wells. The flowmeters measure voltage, which is proportional to the flow. The meters are capable of measuring flow rates as low as 100 mL/cm in the laboratory, but realistically measure rates on the order of several hundred mL/cm in the field. The meters are 1 inch in diameter and are equipped with a packer to isolate the zone to be metered. The meter can be connected to a computer for real-time data collection and an analog to digital converter. The meter measures the vertical component of flow in the borehole. To measure the flow into the well solely due to pumping, the measured flow must be corrected for ambient flow into the well.

Further information on the use of borehole flowmeters for site characterization can be found in "Site Characterization Methods for the Design of In-Situ Electron Donor Delivery Systems," a paper submitted for the Proceedings of the 1997 Battelle Conference (Acree, 1997).

Monitoring for Integration of Hydrologic, Biologic, and Chemical Characterization, Biological Characterization

Guy Sewell (SPRD-Ada) presented the monitoring needs for the biological characterization of a site. Additional information on his presentation is pending. For more information at this time, he can be contacted at the R.S. Kerr Laboratory at 405-436-8566 .

Monitoring for Integration of Hydrologic, Biologic, and Chemical Characterization, Geochemical Characterization

Puls compared the DMLS multi-layer sampling system to conventional monitoring wells for the estimation of the extent of ground-water contamination. He pointed out the advantages of using DMLS instead of wells. He had a DMLS sampler on hand as an example. Puls distributed copies of a paper that appeared in volume 25 of the *Journal of Contaminant Hydrology* entitled "Multi-layer sampling in conventional monitoring wells for improved estimation of vertical contaminant distributions and mass" (Puls and Paul, 1997). Additional copies can be obtain from Puls. Contact him at 405-436-8543.

THURSDAY, JULY 31, 1997

GROUND-WATER FORUM SESSION

Subsurface Extraction Research at Hill Air Force Base (AFB)

Project Overview

Carl Enfield (SPRD-Ada) summarized the research on subsurface extraction techniques conducted by EPA and DOD at Hill AFB near Salt Lake City, Utah. The goal of the research was to compare various extraction techniques to clean up LNAPL in ground water. The LNAPL contaminated the ground water at the operable unit as a result of past usage of chemical waste pits and a fire training area. The test site occupies six acres.

Nine isolated demonstration cells (similar to the Waterloo design) were constructed of sheet pile welded with outside angle iron. The demonstration cells, which were 5 meters long by 3 meters wide were grouted to a depth of 35 feet. The nine extraction techniques tested at the cell were:

1) cosolvent solubilization
2) cosolvent mobilization
3) air sparging/SVE
4) in-well aeration
5) steam injection
6) complex sugar solubilization
7) surfactant solubilization
8) surfactant middle phase microemulsion
9) single phase microemulsion

Performance evaluation of the extraction techniques included soil sampling, ground-water sampling, and partitioning tracer tests both prior to and after implementation of the technique. In addition, a mass balance was conducted to calculate the mass removal for each process stream.

In summary, Enfield said that the results of the performance evaluations indicated that in-well aeration was considered better for dissolved contaminants and was not recommended for NAPL. Enhanced volatilization by steam injection removed a lot of the undecane, and the contaminant mass was reduced considerably; however, some hotspots remained. Complex sugar solubilization was determined to be an ineffective extraction method. Surfactant mobilization, cosolvent mobilization, and surfactant middle phase microemulsion were more effective techniques that removed most of the undecane.

Ben Blaney (ORD/NRMRL/Cincinnati) asked whether other factors, such as economics or applicability, indicate which technique should be pursued. Enfield replied the all of the techniques can be used to extract contaminants from a permeable subsurface. He said that the techniques selected will depend on the contaminants present. He added that more evaluations need to be conducted outside of the demonstration cells.

Site Characterization

Lynn Wood (ORD/NRMRL/SPRD-Ada) summarized the characterization of the site and source area conducted prior to implementing the subsurface extraction techniques at Hill AFB. He explained that characterization was conducted on three scales: 1) the operable unit; 2) the study area; and 3) the demonstration cells.

To characterize the operable unit, researchers reviewed available historical information. They analyzed the NAPL, conducted a ground penetrating radar survey, and cored soil samples. Hundreds of contaminants were identified at the operable unit, but the following NAPL analytes were targeted:

1) decane
2) undecane
3) toluene
4) naphthalene
5) o-xylene
6) m- and p-xylenes
7) TCE
8) 1,1,1-TCA
9) 1,2-dichlorobenzene
10) 1,3,5-trimethylbenzene

The operable unit was found to be underlain by a sand and gravel aquifer, ranging from a gravelly sand to a sandy gravel. A clay layer was identified 20 to 30 feet below ground surface.

The objective of the study area characterization was to confirm the presence of NAPL and to locate the clay aquitard for emplacement of the demonstration cells. Ground penetrating radar and resistivity surveys were conducted, and cores were sampled using hollow stem augers. The samples were extracted on site to avoid volatilization of contaminants.

The objective of the demonstration cell characterization was to determine the hydrodynamic and geochemical properties of the cells, as well as the distribution and chemistry of the NAPL. The results were used for experimental design and performance monitoring. The

methods used to characterize the demonstration cells included core sampling, static and dynamic ground-water sampling, non-reactive tracer tests, partitioning tracer tests, and interfacial tracer tests.

Wood explained that the tracer tests were conducted to assess the hydrodynamics of the subsurface. The partitioning tracers partition between NAPL and water in a known manner, so tracers can be used to determine whether NAPL is present. A suite of conservative and non-conservative tracers with NAPL/water partition coefficients ranging from 0 to 40 were injected into a well. The ground water was monitored at several points between the injection well and extraction well. The partitioning tracer tests make several assumptions: that retardation of the tracer is due to partitioning into the NAPL phase; the NAPL/water partition coefficients are independent of tracer concentrations; there is no mass transfer coefficient; and the hydraulic flow field effectively contacts all of the NAPL in the region of interest.

Interfacial tracers accumulate in the NAPL/water interface. The interfacial tracer tests make several assumptions: the tracer adsorbs at the interface, but does not partition into the NAPL phase; adsorption occurs as monolayer coverage; and each tracer molecule occupies a constant known molecular area at the interface.

Steve Hutchins (ORD/NRMRL/SPRD-Ada) asked whether the vibrations occurring during the installation of sheet piling caused settling of the subsurface and as a result, affected accessibility to the source area. Wood indicated that settling did occur, and this likely affected accessibility.

Cosolvent Mobilization

Ron Falta (Clemson University) explained the theory behind cosolvent mobilization and then summarized the results of the cosolvent mobilization demonstration cell. Falta said that cosolvents are miscible solvents (like alcohol) and have operational mechanisms similar to surfactants. They are applied to the site as cosolvent “floods.” He later described the phase behavior of cosolvent systems and noted mechanisms to minimize and maximize DNAPL mobilization. Falta concluded that as in the oil field practice, the existing fraction flow theory correctly predicts the behavior of cosolvent floods.

A cosolvent flood of 85 percent tertbutyl alcohol (TBA) and 15 percent hexanol was used for the demonstration at Hill AFB. Hexanol was added to make the solution more efficient because a pure solution of TBA freezes at room temperature. Three injection wells, three extraction wells, and 11 multi-level samplers were installed. The results of the multi-level sampling following the cosolvent flood showed a reduction to 3 percent NAPL saturation. The percent reduction in NAPL averaged 80 percent at the samplers. The target analytes exhibited a similar total removal (78.1 percent), although higher reductions were achieved for the more soluble compounds. Falta concluded that it is technically feasible to mobilize and remove LNAPLs using cosolvents.

Willey asked Falta whether there is an advantage to phasing the use of cosolvents. Falta replied that there is an advantage to phasing in the application of cosolvents because it “softens” the mobilization.

Microemulsions

Mike Annable (University of Florida) described the use of cosolvent flushing and microemulsions to extract LNAPL at two of the Hill AFB demonstration cells. A cosolvent made up of 70 percent ethanol and 12 percent pentanol was used. The pentanol was added to aid in solubilizing the NAPL found at the site. Because alcohol is less dense than water, it was expected to stay largely in the upper zone of contamination. To introduce alcohol into the lower zone of contamination, a flushing gradient was induced.

The cosolvent was pumped through the demonstration cell and extracted to waste tanks. The removal of NAPL was measured by analyzing soil cores. Analysis of the soil cores indicated that a larger percentage of target analytes was removed from the top of the test cell (80 to 90 percent) than the bottom (75 percent).

In a second cell, a mixture consisting of 3 percent surfactant (Brig-97) and 2.5 percent alcohol was introduced to the aquifer to generate a microemulsion to mobilize the NAPL. Analysis of soil cores showed substantial removal of the target analytes (87 to 96 percent reduction). The tracer data collected at the extraction wells showed a 69 percent removal along the sides of the demonstration cell and a 79 percent removal at the center.

The NAPL mass removal effectiveness of the cosolvent flushing and microemulsion extraction techniques were compared based on the results of: 1) partitioning tracer tests; 2) extraction well mass balances; and 3) soil core analyses. Cosolvent flushing yielded removals of 81 percent, 87 percent, and 88 percent for the three methods, respectively; the microemulsion removals were 74 percent, 93 percent, and 95 percent.

Although the results of the two techniques are fairly comparable, microemulsions appear to have been more effective from a constituent basis. Another factor in the comparison is economics. The cost of the cosolvent mixture was $2.50 per gallon, versus $1.25 per gallon for the microemulsion mixture. The relative cost of waste disposal for the two methods has not been assessed yet.

Vince Mallott (Region 6) asked if the number of pore volumes needed to achieve complete removal was projected. Annable estimated that 15 to 20 pore volumes would be required. Wilson inquired about the cost of the mixtures per cubic yard of treated soil, but Annable indicated that the cost had not been calculated. In response to a question regarding the recovery of the surfactant, Annable indicated that he could not answer how much had been removed. He noted, however, that there was some degradation of the surfactant after injection of the pentanol ceased.

Surfactant Solubilization

David Sabatini (University of Oklahoma) summarized the results of the surfactant solubilization demonstration. He explained that because the NAPL is trapped by capillary forces, it would take a lot of water to flush the NAPL without the addition of surfactant to increase contaminant solubility. He indicated that some surfactants are water soluble (Windsor Type I surfactant) and others are oil soluble (Windsor Type II surfactant). Adding sodium chloride to a water soluble ionic surfactant lowers its effective HLB to produce an intermediate Windsor Type III surfactant. Furthermore, adding a hydrotrope to a Windsor Type II surfactant raises its effective HLB and will also produce a Type III surfactant.

Sabatini said that the use of surfactant stabilization is more economical at smaller sites. Surfactant solubilization is limited to the sources zone where there is residual saturation, and mobilization of the NAPL is preferred over solubilization. Recovery and reuse of the surfactant will make this extraction technique more economical.

The design of a surfactant solubilization system should be based on a review of literature, laboratory studies, and field studies. Sabatini suggested examining five to eight surfactants in the laboratory and assessing ground water/soil/contaminant interactions with the surfactants. He also suggested conducting column studies with two or three surfactants. Sabatini mentioned problems with mixing and dispensing the surfactant at Hill AFB, due to the cold weather conditions.

Sabatini noted that surfactants in combination with water and air cause foaming. To avoid foaming, the liquid loading rate and the liquid/air ratio can be adjusted. Both packed tower and hollow fiber methods of removing VOCs from surfactants were tested at the operable unit. Sabatini pointed out that VOCs must be removed in order to reuse the surfactant. A comparison of the two methods showed that the packed tower removed 90 to 95 percent of the TCE and 80 to 90 percent of the PCE; the hollow fiber removed 98 to 100 percent of the TCE and 80 to 90 percent of the PCE.

In summary, Sabatini concluded that surfactant mobilization is a more efficient approach to LNAPL extraction than surfactant solubilization. He stressed the importance of sweep efficiency in the process and the need for additional field demonstrations at sites with different geology and contaminants. Perhaps mobilization can be coupled with other processes to achieve clean-up goals. He added that surfactant decontamination is highly efficient using design equations and operational guidelines.

Willey asked whether the technique poses a problem because DNAPL can solubilize and migrate. Sabatini indicated that ideally, one would design an extraction system with an ultra-high solubilization, in addition to decreased surface tension. If the mobilized DNAPL can be captured at depth, then gravity can be used to supplement the system.

A person asked whether the alcohol used to mobilize the NAPL could kill the microorganisms that aid in degradation of contaminants. Wilson indicated that alcohol sterilizes surfaces, and there are too many nooks and crannies in the soil for the alcohol to reach all of the microorganisms. Willey suggested that biodegradation could be used as a polishing step to treat remaining ground-water contaminants after the NAPL is extracted.

Willey mentioned that there is an upcoming neutral buoyancy surfactant flush experiment at a site in New Hampshire. The site has received a consent decree to stop all migration of contaminants in 30 years. Willey can be contacted for further information on the experiment.